APR 1 5 1998

MEMORANDUM

SUBJECT:

Section 18 Emergency Exemption - Use of Pyridate on Garbanzo Beans

(Chickpeas) in Washington State to Control Broadleaf Weeds (D244668,

PC Code# 128834, ID # 98WA0031)

FROM:

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THRU:

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TO:

Robert Forrest, PM 05,

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Registration Division

A. SUMMARY

ERBII/EFED concurs with the proposed emergency use of pyridate on garbanzo beans in Washington to control broadleaf weeds. Pyridate is not expected to pose a threat to ground water, and under normal use pyridate is not expected to reach surface water. In addition, EFED concludes that because of the limited acres to be treated (6,000) and the product to be used (10,800 lbs. ai) the environmental risk is minimal. However, an endangered plant species, Water Howellia, that inhabits Spokane county has been identified as a possible "may effect".

B. SUBMISSION PURPOSE

The State of Washington is requesting an emergency exemption under section 18 of FIFRA to use pyridate on garbanzo beans to control broadleaf weeds. This is the second year this use has been requested. Pyridate is a post-emergence contact herbicide that is currently used in Europe and Asia to control broadleaf and some grassy weeds in a variety of crops. The mode of action is understood to be inhibiting photosynthesis. An EUP was granted by EPA in 1987.



C. USE INFORMATION

Application: By ground equipment only, from April 13 - June 26, 1998 in Central Basin and

Walla Walla region of counties; and from May 2 - July 15, 1998 in Palouse

area.

Rates: 0.9 lb. a.i. per acre (2 pints of product), two applications per season at least 20

days apart.

Total area: 6,000 acres in Washington.

Total pounds: At the maximum allowable use of 2 applications of 2 pints (0.9 lbs. a.i. per

acre) on 6,000 acres, a total of 3,000 gallons of formulated product (10,800 lbs.

a.i.) may be used.

D. USE RESTRICTIONS

1.) Do not apply by air.

2.) Do not apply through any type of irrigation system.

3.) Application may not be made within 60 days of harvest.

4.) Do not allow livestock to graze on treated fields. Do not feed forage, hay or silage from treated fields to livestock.

E. ENVIRONMENTAL ASSESSMENT

1. Environmental Fate Assessment

Pyridate generally degrades rapidly in the environment to form several minor degradates (unidentified) and one major degradate, CL-9673, which is more stable than the parent.

Pyridate hydrolyzes rapidly with half lives of 66.7, 17.8, and 6.8 hours at pH 5, 7, and 9, respectively. The degradate, CL-9673, is relatively stable to hydrolysis with a reported half life of >35 days (>95% remained as CL-9673 after 35 days).

Pyridate does not undergo any significant aqueous or soil photolysis, but is rapidly hydrolyzed to CL-9376, which is readily photolyzed in water with a half life of 3.7 to 14 days and on soil with a half life of 16 days. These half lives suggest that pyridate and its primary degradate will be short lived in the environment when exposed to sunlight. Cl-9376 has a terrestrial field dissipation half life of 7-29 days.

In anaerobic conditions, the degradate is persistent with a half life for anaerobic soil metabolism of 330-630 days. The soil partition coefficient (Kd) for CL-9673 is 0.3-3.5, showing it has the potential to leach to ground water.

Neither pyridate nor CL-9673 is volatile. A fish study showed that pyridate bioaccumulates (464 times), but 99% of residues were eliminated in 14 days.

In summary, the data shows that in terrestrial and aquatic environments, pyridate rapidly hydrolyzes to CL-9673 with half lives usually ≤3 days. Although pyridate is also rapidly hydrolyzed under anaerobic soil conditions to CL-9673, CL-9673 is persistent and undergoes very little degradation with half lives from 330-630 days in anaerobic soil conditions. Aerobic half lives of CL-9673 are about 10-30 days in soils. CL-9673 is rapidly degraded under the influence of light as showed by the 14 day half life in the water and 16 day half life in soil. Overall, pyridate and its primarily degradate, CL-9673, will not persist in aerobic conditions, while CL-9673 will persist in anaerobic conditions.

SURFACE WATER ASSESSMENT:

The GENEEC model was used to estimate surface water concentrations for pyridate. Garbanzo beans (chick peas) were used as the crop of interest. The modeling results show that pyridate has the potential to move into surface waters, especially during times of unusually heavy rainfall.

The peak GENEEC estimated environmental concentration (EEC) of pyridate in surface water is 97 ppb (Table 1). This estimate is based on a maximum application rate of 0.9 lb. ai/acre. The GENEEC values represent upper-bound estimates of the concentrations that might be found in surface water due to pyridate use.

GENEEC (USEPA, 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data that is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to 1 and 5% of the applied rate for ground and aerial spray application, respectively.

GENEEC is not an ideal tool for drinking water risk assessments. Surface water sources of drinking water tend to come from bodies of water that are substantially larger than a 1-hectare pond. Furthermore, GENEEC assumes that essentially the whole basin receives an application of the chemical. In virtually all cases, basins large enough to support a drinking water facility will contain a substantial fraction of area that does not receive the chemical. Furthermore, there is always at least some flow (in a river) or turn over (in a reservoir or lake) of the water so the persistence of the chemical near the drinking water facility is usually over estimated by GENEEC. Given all this, GENEEC does provide an upper bound on the concentration of pesticide that could be found in drinking water and therefore can be appropriately used in screening calculations. If a risk assessment performed using GENEEC output does not exceed

the level of concern, then one can be reasonably confident that the risk will also be below the level of concern. However, since GENEEC can substantially overestimate true drinking water concentrations, refining the GENEEC estimate will be necessary if the level of concern is exceeded. The input values for GENEEC are listed in Table 2. GENEEC version 1.2 was used for the calculations.

Table 1. GENEEC EECs (µg/L) for Pyridate Use on Garbanzo Beans

Crop	Peak GEEC	4 Day GEEC	21 Day GEEC	56 Day GEEC
Garbanzo beans	97 .	95	88	75

Table 2. GENEEC Environmental Fate Input Parameters for Pyridate

DATA	VALUE
Application rate	0.9 lb ai/A (label)
Maximum number of application per year	2 (label)
Interval between applications	20 days (label)
Soil organic carbon coefficient (Koc)	3 (lowest computed for three soils) ¹
Soil aerobic metabolism (maximum value)	210 days (261827)
Solubility	1.5 ppm (one liner database)
Aerobic aquatic metabolism half life	75 days(one liner, supplemental study)
Photolysis half life	14.1 days(40939103)

 $^{^1}$ See Table 3 for data used to compute $K_{\!\scriptscriptstyle DC}$ values

GROUND WATER ASSESSMENT

Data show that the parent compound, pyridate, does not possess the environmental fate parameters associated with a compound that could leach to ground water. However, the fate parameters of the degradate, CL-9673, do seem to show that it has the potential to leach to ground water (K_d of 0.3 - 3.5), especially in soils of low organic matter. An EFED to RD memo of July 6, 1992 requested a prospective ground water study to investigate this possibility, although no such study was conducted as far as known. An earlier review of fate data by EFED (June 29, 1992) concluded that pyridate and CL-9673 probably have limited potential to move downward in the soil profile. This conclusion was substantiated in a field dissipation study in which no detections of CL-9673 were made at depths greater than 12 inches. Although the data shows that CL-9673 is not tightly bound to soil and has the potential to leach, it likely could be degraded by aerobic processes in the soil before it can move appreciably. This was shown by a study where CL-9673 was initially detected below 6 inches, but no residues were detected after the fifth day following application. In unusual condition such as flooding, where anaerobic conditions existed in the top soil layers for up to 60 days, CL-9673 could persist and possibly leach to ground water or run off to surface water.

Pyridate is not listed in the EPA Pesticides in Ground Water Database, nor is there an EPA MCL or health advisory.

Table 3 shows the input parameter values used in SCI-GROW for pyridate and the resulting estimated ground water concentration.

Table 3. SCI-GROW Environmental Fate Input Parameters for Pyridate

Average K _{oc} (I/kg) ¹	64.5
Application rate (lb a.i./acre)	0.9
Number of applications per year	2
Use rate (maximum total/season)	1.8 lb ai/A
Aerobic soil metabolism half-life (days)(average)	105
Relative intrinsic leaching potential	4.9
Estimated groundwater concentration	4.44 ppb

¹ The K_{oc} used as model input was computed from three Kd values for three soils of different organic carbon. The K_d values were 0.37, 2.3, and 0.3 with % organic carbon of 0.48, 2.66, and 1.0, respectively. This gave K_{oc} values of 77,86.5, and 30, for an average K_{oc} of 64.5. Use of the average K_{oc} value gave an estimated ground water concentration of 4.44 ppb. Use of the median K_{oc} gave an estimated ground water concentration of 3.6 ppb. To be conservative, the average K_{oc} value was used to compute EEC. Note that even though K_{oc} was used in model, no significant correlation (at 95% level) was found between organic carbon and K_d .

EFED estimates a drinking water exposure concentration of 4.44 ppb for pyridate as predicted by SCI-GROW modeling results. There may be exceptional circumstances under which groundwater concentrations could exceed the SCI-GROW estimates. However, such exceptions should be quite rare since the SCI-GROW model is based exclusively on maximum groundwater concentrations from studies conducted at sites and under conditions that are most likely to result in groundwater contamination. The groundwater concentrations generated by SCI-GROW are based on the largest 90-day average recorded during the sampling period. The concentration (4.44 ppb)can be considered as both the acute and chronic values.

2. Ecological Risk Assessment

a. Toxicity Data

Pyridate is practically nontoxic to birds on a dietary basis ($LC_{50} > 5000$ ppm for mallard and bobwhite), but slightly toxic on an acute oral basis ($LD_{50} > 1269$ and 1505 mg/kg for bobwhite). Avian Reproduction studies show NOEL to be 1600 ppm for bobwhite and 640 ppm for mallard.

HED's Mammalian studies show that pyridate is practically nontoxic (LD50 = 3544 mg/kg). The 3-generation rat study show the NOEL = 216 ppm.

Pyridate is moderately toxic to freshwater fish ($LC_{50} > 1.2$ ppm) and aquatic invertebrates

(LC₅₀ = 1.08 ppm), highly toxic to estuarine fish and clams (LC₅₀ > 0.3 and 0.145 ppm, respectively), and moderately toxic to shrimp (LC₅₀ = 3.8 ppm). The only toxicity data available on the primary degradate, CL-9673, is an LC₅₀ = 26 ppm for an aquatic invertebrate, Daphnia.

There are no data available to provide a risk assessment to non-target plants.

b. Risk Assessment

Aquatic

The Risk Quotients (RQ) are derived by dividing the exposure value by the toxicity value. To determine aquatic exposure, a computer tier I model, GENEEC, was used. The estimated peak concentrations in an aquatic environment would be 97 ppb.

The aquatic Risk Quotients (RQ) are as follows:

Fish	0.08
Aquatic invertebrates	0.09
Estuarine fish	0.32
Shrimp	0.03
Oysters (Clams)	0.67

The freshwater fish LC₅₀ cannot be determined at the solubility level. Therefore, minimal risk is assumed for fish. The Level of Concern (LOC) has been exceeded for endangered species for freshwater invertebrates, estuarine fish and clams/mussels. The LOC has also been exceeded for consideration as a restricted use candidate for estuarine fish and clams/mussels.

Although the LOC has been exceeded for restricted use and endangered species, the LOC exceedances are uncertain for the following reasons:

- The GENEEC-run concentrations may be more reflective of the pyridate degradate, CL-9673, since the parent pyridate tends to degrade to Cl-9673 rapidly. Toxicity data for CL-9673 are not available for freshwater fish and estuarine species.
- The aquatic toxicity tests were conducted under static conditions. The static conditions may have initial toxicity of the parent pyridate and later have toxicity of the degradate, CL-9673. It is uncertain what chemical the organisms may have been exposed to for the duration of the time. CL-9673 toxicity data on Daphnia show that Cl-9673 may be less toxic than the parent pyridate on aquatic organisms however, this is uncertain due to lack of toxicity data on CL-9673.
- Pyridate is insoluble in water at approximately 1.5 ppm. The LC₅₀ for rainbow trout is greater than the highest concentration tested. About 40% of the fish were dead at the highest concentration. The bluegill study showed no mortality at the highest

concentration tested (2.1 ppm). Since the LOC for freshwater fish is very marginal, it is the opinion of the reviewer that minimal risk can be expected.

• Pyridate is insoluble in water at approximately 1.5 ppm. The LC₅₀ for estuarine fish is greater than the highest concentration tested. There are no mortalities found at the highest concentration tested in estuarine fish study. This lack of mortality may show that the LOC exceedances may be much lower than estimated.

There are no chronic data available to provide chronic risk assessment for aquatic species.

Terrestrial

The exposure for terrestrial animals is usually determined by the Kenaga/Fletcher nomogram. The highest terrestrial residue anticipated is determined by multiplying the residues found on short grass (240 ppm) after application of 1 lb ai/A with the application rate (0.9 x 2 applications) resulting in 432 ppm. The RQ is then divided by the toxicity endpoint. The following RQ's were calculated for terrestrial animals:

Birds 0.09 Mammals 0.01

The terrestrial chronic RQ are as follows:

Birds 0.68 Mammals 0.32

There are no LOC exceedances for the terrestrial animals.

Plants

Since there are no plant toxicity data available, no plant risk assessment can be done. Therefore, a default assumption is that terrestrial and aquatic non-target plants (including endangered species) will be adversely affected from the labeled use of pyridate.

Endangered Species

The following endangered fish species may inhabit counties where pyridate is to be used on chickpeas:

Chinook Salmon (Snake River), Snake River Sockeye Salmon, Steelhead (Upper Columbia River population), and Bull Trout (Columbia River population).

After consulting with OPP's Endangered Species Protection Program, it was agreed that the endangered fish species will not be affected by the labeled use of pyridate because of the very low LOC exceedances for endangered fish species and the streams and rivers where these

species are found are rapid and large. The exposure of these fish species to pyridate will not be enough to warrant a concern.

However, there is a concern for the endangered plant species, Water Howellia, in Spokane county. Measures must be taken to ensure the protection of this species in Spokane county from pyridate by contacting Washington state endangered species program and/or the U.S. Fish and Wildlife Service.

F. Ground Water Impact

Data show that the parent compound, pyridate, does not possess the environmental fate parameters associated with a compound that could leach to ground water. However, the fate parameters of the degradate, CL-9673, do seem to show that it has the potential to leach to ground water (Kd of 0.3 - 3.5), especially in soils of low organic matter. An EFED to RD memo of July 6, 1992, requested a prospective ground water study to investigate this possibility, although no such study was conducted as far as known. An earlier review of fate data by EFED (June 29, 1992) concluded that pyridate and CL-9673 probably have limited potential to move downward in the soil profile. This conclusion was substantiated in a field dissipation study in which no detections of CL-9673 were made at depths greater than 12 inches. Although the data shows that CL-9673 is not tightly bound to soil and has the potential to leach, it is likely it will be degraded by aerobic processes in the soil before it can move appreciably. This was substantiated by a study where CL-9673 was initially detected below 6 inches, but no residues were detected after the fifth day following application. In unusual condition such as flooding, where anaerobic conditions existed in the top soil layers for up to 60 days, CL-9673 could persist and possibly leach to ground water.

G. Surface Water Impact

Available data show that pyridate and it primary degradate degrade rapidly by hydrolyses and photolysis and would not be expected to create a surface water contamination problem. However, if run-off were rapid, taking less time than the aqueous photolysis half life of up to 14 days, such as following a heavy rain, and CL-9673 was discharged to surface water with anaerobic conditions, it then could persist for a significant length of time of 1.5 to 2.5 years. (An anaerobic aquatic half life is not known, but can be estimated from the anaerobic soil metabolism value to be 1.5 to 2.5 years).

Peer reviewed by: Bety gin 5/5/98

GENEEC MODEL VERSION 1.2 PRINTOUT

RUN No. 1 FOR pyridate INPUT VALUES

RATE (#/AC) APPLICATIONS SOIL SOLUBILITY % SPRAY INCORP ONE(MULT) NO.-INTERVAL KOC (PPM) DRIFT DEPTH(IN)

.900(1.743) 2 20 3.0 1.5 1.0 .0

FIELD AND STANDARD POND HALFLIFE VALUES (DAYS)

METABOLIC DAYS UNTIL HYDROLYSIS PHOTOLYSIS METABOLIC COMBINED (FIELD) RAIN/RUNOFF (POND) (POND-EFF) (POND) (POND)

210.00 0 N/A 14.10-1730.07 75.00 71.88

GENERIC EECs (IN PPB)

PEAK AVERAGE 4 AVERAGE 21 AVERAGE 56 GEEC DAY GEEC DAY GEEC DAY GEEC

96.72 95.33 87.90 74.93

SCIGROW VERSION 1.0 PRINTOUT

RUN No. 1 FOR PYRIDATE INPUT VALUES

APPL (#/AC) APPL. URATE SOIL SOIL AEROBIC RATE NO. (#/AC/YR) KOC METABOLISM (DAYS)

.900 2 1.800 64.5 105.0

GROUND-WATER SCREENING CONCENTRATIONS IN PPB

4.436610

A= 100.000 B= 69.500 C= 2.000 D= 1.842 RILP= 4.316 F= .392 G= 2.465 URATE= 1.800 GWSC= 4.436610

REFERENCES:

Barrett, M. Proposal For a Method to Determine Screening Concentration Estimates for Drinking Water Derived from Ground Water Studies. EFED/OPP. September 20, 1997.

- U.S. Environmental Protection Agency. National Pesticide Survey. Office of Water. OPTS. 1990.
- U.S. Environmental Protection Agency. 1992. Pesticides in Ground Water Database A Compilation of Monitoring Studies: 1971 1991. Office of Prevention, Pesticides, and Toxic Substances, EPA 734-12-92-001, September 1992.
- U.S. Environmental Protection Agency. 1995. GENEEC: A Screening Model for Pesticide Environmental Exposure Assessment. The International Symposium on Water Quality Monitoring, April 2-5 1995. American Society of Agricultural Engineers. p 485.
- U.S. Environmental Protection Agency. 1996. Drinking Water Regulations and Health Advisories. USEPA Report. U.S. Government Printing Office, Washington, DC.